

*The Adsorption of Gases at Low and Moderate Concentrations.*  
 Part III.—*Experimental Verification of the Constants in the*  
*Theoretical Adsorption Isostere.*

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(Communicated by Prof. JAMES WALKER, F.R.S. Received July 22, 1919.)

PART III.

Having established the form of the theoretical isosteres and isotherms, it is now possible and desirable to find how far the constants of the deduced expressions fall in with their theoretical values. We will in the present paper confine ourselves to a consideration of the constants A and B of the *zero* isostere. These are given by equation (7) in

$$\log \left( \frac{\alpha}{c} \right)_{\alpha=0} = B(0) + \frac{A(0)}{T}$$

and they are also given by  $A_0$  in equation (8),

$$\log \alpha/c = A_0 - A_1 \alpha$$

since

$$A_0 = B(0) + \frac{A(0)}{T}.$$

(a) *Miss Homfray's Observations.\**

There exists only one set of observations sufficiently extensive to be suitable for our present purpose.

Miss Homfray's observations embrace the adsorption by cocoanut charcoal of helium, argon, nitrogen, carbon monoxide, methane, carbon dioxide, and ethylene, and it has been found possible to evaluate  $A_0$  for all these gases at various temperatures. Accurate extrapolation from the observations was sometimes difficult in the case of the first two gases which show many irregularities in the data, but was relatively easy with the others. Fig. 4 represents graphically the extrapolation in the case of ethylene, and illustrates the power and scope of the method adopted. It is, of course, obvious that the further away from  $\alpha = 0$  the observations lie, the less reliable is the extrapolation, and the assumption has been made that there is no change in curvature in the graphs near  $\alpha = 0$ , since such is not found in the case of those curves with values available near  $\alpha = 0$ . In extrapolating, repeated use was made of the fact that the gradient of the  $(\alpha, \log \alpha/c)$  curves varies

\* 'Zeit. f. Physik. Chem.,' vol. 74, p. 129 (1910).

continuously with the temperature. This was helpful in the case of observations at low temperatures when few points were available near  $\alpha = 0$ , and

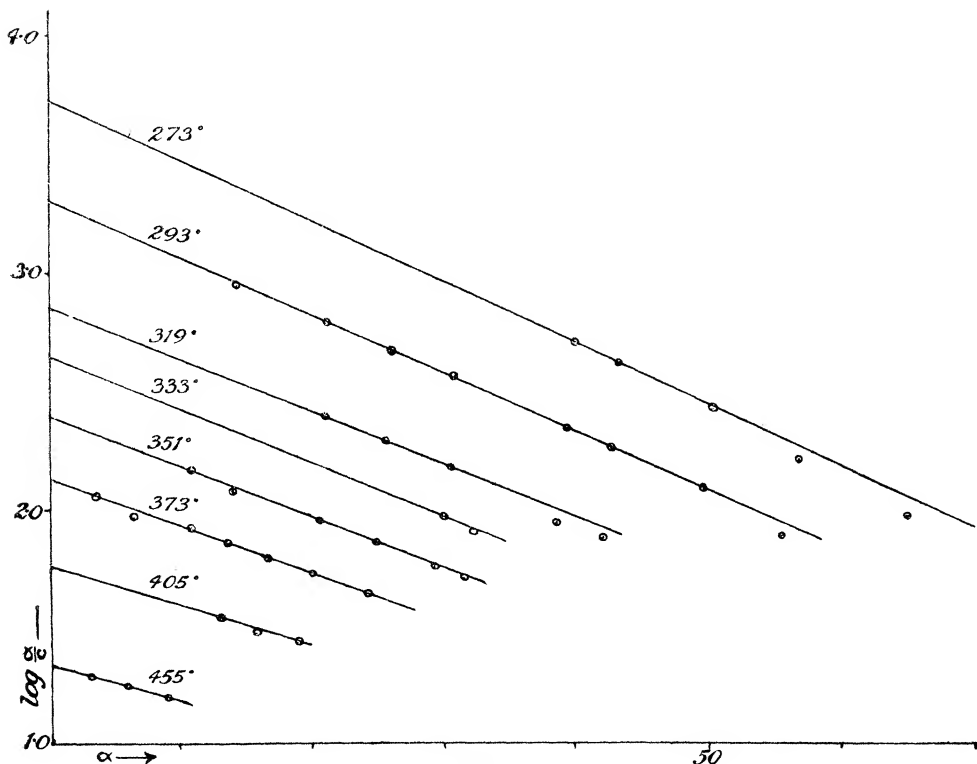


FIG. 4.

was also used at high temperatures where perhaps only one observation was recorded. The error in extrapolating here would be small, since the point was always near  $\alpha = 0$ . But in a few cases the readings are so discordant that only a mean value can be given with a big probable error. This was particularly the case with argon.

The values of  $A_0$  thus obtained have been plotted against the reciprocal of the absolute temperature in order to test (7), and the curves are shown in fig. 5. It will at once be seen that the graphs closely approximate to straight lines, that is,  $A$  and  $B$  are appreciably independent of the temperature over the range studied. This is more closely examined in the Tables following, where a comparison is made of the observed and calculated values of  $\log a/c$  for different temperatures. As regards the constants  $A$  and  $B$ , the difference between  $\log a/c$  calculated and observed is the error in  $B$  if  $A$  is regarded as known, and the last column gives the variation in the

constancy of A when B is regarded as known. The real test of the formula, however, is the percentage error in the calculated value of  $a/c$ .

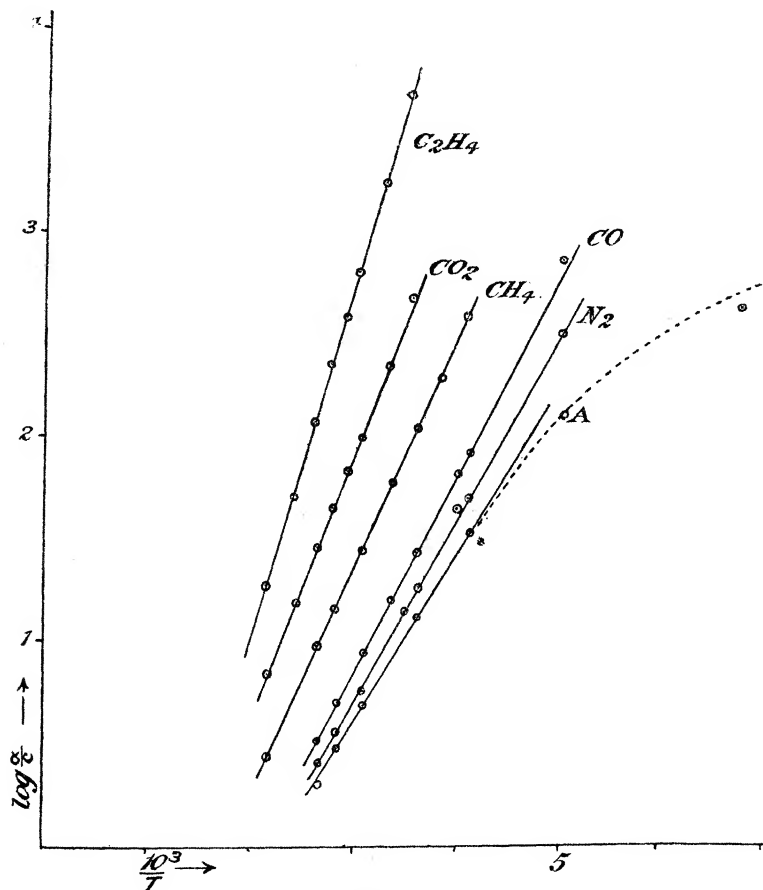


FIG. 5.

Table IX.

Ethylene.  $T_c = 283$ . $B = 3.676$ .  $A = 1631$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
273	3.659	3.651	-0.008	-1.9	1633
293	3.227	3.243	+0.016	+3.8	1627
319	2.792	2.789	-0.003	-0.7	1632
333	2.572	2.574	+0.002	+0.5	1630
351	2.330	2.322	-0.008	-1.9	1634
373	2.057	2.049	-0.008	-1.9	1634
405	1.700	1.703	+0.003	+0.7	1629
455	1.261	1.261	$\pm 0.000$	$\pm 0.0$	1631

Table X.

Carbon dioxide.  $T_c = 304$ . $B = \bar{2} \cdot 085$ .  $A = 1245$ .

T.	Log $\alpha/c$ obs.	Log $\alpha/c$ calc.	Divergence.	Percentage error in $\alpha/c$ .	A calc.
273	2·671	2·656	-0·015	-3·5	1249
293	2·343	2·344	+0·001	+0·2	1245
319	1·987	1·998	+0·011	+2·6	1241
333	1·822	1·834	+0·012	+2·8	1241
351	1·646	1·641	-0·005	-1·2	1246
373	1·445	1·433	-0·012	-2·8	1249
405	1·174	1·169	-0·005	-1·2	1247
455	0·828	0·831	+0·003	+0·7	1244

Table XI.

Methane.  $T_c = 178$ . $B = \bar{2} \cdot 068$ .  $A = 1081$ .

T.	Log $\alpha/c$ obs.	Log $\alpha/c$ calc.	Divergence.	Percentage error in $\alpha/c$ .	A calc.
240	2·583	2·572	-0·011	-2·6	1084
255	2·295	2·307	+0·012	+2·8	1078
273	2·038	2·028	-0·010	-2·3	1084
293	1·774	1·757	-0·017	-4·0	1086
319	1·440	1·456	+0·016	+3·8	1075
351	1·151	1·147	-0·004	-0·9	1082
373	0·967	0·966	-0·001	-0·2	1081
455	0·439	0·444	+0·005	+1·2	1079

Table XII.

Carbon monoxide.  $T_c = 132$ . $B = \bar{2} \cdot 014$ .  $A = 933$ .

T.	Log $\alpha/c$ obs.	Log $\alpha/c$ calc.	Divergence.	Percentage error in $\alpha/c$ .	A calc.
194·7	2·865	2·806	-0·059	-14·6	944
239·4	1·908	1·911	+0·003	+0·7	932
244·5	1·815	1·830	+0·015	+3·5	929
273	1·427	1·431	+0·004	+0·9	932
293	1·196	1·198	+0·002	+0·5	932
319·2	0·935	0·935	$\pm 0 \cdot 000$	$\pm 0 \cdot 0$	933
351	0·697	0·672	-0·025	-5·9	941
373	0·515	0·516	+0·001	+0·2	933

Table XIII.

Nitrogen.  $T_c = 127$ . $B = \bar{2} \cdot 110$ .  $A = 856$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A calc.
194.7	2.509	2.506	-0.003	-0.7	857
239.4	1.688	1.686	+0.003	+0.7	855
244.5	1.641	1.611	-0.030	-7.2	863
273	1.249	1.245	-0.004	-0.9	857
282.3	1.140	1.143	+0.003	+0.7	855
306.5	0.899	0.904	+0.005	+1.2	855
320	0.749	0.785	+0.036	+8.6	844
351.2	0.557	0.548	-0.009	-2.1	859
373	0.409	0.405	-0.004	-0.9	857

Table XIV.

Argon.  $T_c = 156$ . $B = \bar{2} \cdot 11$ .  $A = 822$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	A calc.
145	(2.6?)	3.78	(651)
195	2.06-2.12	2.33	770-782
236	1.50-1.55	1.59	800-811
273	1.124	1.12	823
321	0.67-0.71	0.67	822-835
351	0.43-0.53	0.45	815-850
373	0.23-0.31	0.31	791-821

The values of A and B for argon given in Table XIV were not deduced directly from the graph, owing to the difficulty in evaluating  $A_0$ . They were deduced by extrapolation from the values for A and B obtained from the isosteres for finite adsorptions tabulated by Miss Homfray. (See, for example, Table I, Part II.)

From the Tables it will be seen that A and B are appreciably constant over a range of some 200 degrees Centigrade, and this indicates from the theoretical discussion that in the region of temperature in question  $r_0$  and  $w$  are appreciably constant, that is, the range of cohesive forces is appreciably constant. The values for argon would, however, indicate that at lower temperatures  $w$  increases. This must be interpreted to mean that the molecule is less closely held to the attracting surface at low temperatures. The curves are, therefore, only *approximately* straight lines, and we are at present unable to predict whether they will remain so at higher temperatures.

Let us now examine a little more closely the physical meaning of the constants A and B. From the theoretical equations of Part I

$$A = \mu/R \cdot a^{\frac{1}{2}} a_0^{\frac{1}{2}} \phi(r_0).$$

For the same adsorbing surface  $A/a^{\frac{1}{2}}$  is proportional to  $\phi(r_0)$ , and if the mean distance  $r_0$  is closely the same for different substances, then  $\phi(r_0)$  is closely the same.  $a^{\frac{1}{2}}$  represents the specific attraction of the adsorbed substance, while the cohesion represents the attraction of the substance for itself and should therefore be proportional to  $a^{\frac{1}{2}} \times a^{\frac{1}{2}}$  or  $a$ . We may take the  $a$  of Van der Waal's equation

$$(p + a/v^2)(v - b) = RT$$

to give us a measure of the cohesion factor of different substances. In the Table following this value of  $a$  has been used and is the mean of the values calculated from observations and given in Landolt-Börnstein's tables, save in the case of helium, where the data of Onnes\* have been employed. The last

Table XV.

Substance.	$a$ .	$a^{\frac{1}{2}}$ .	$A$ .	$A/a^{\frac{1}{2}}$ .
He	0.000069	0.0083	134	$1.61 \times 10^4$
A	0.00259	0.0508	822	1.62
N <sub>2</sub>	268	518	856	1.65
CO	280	529	933	1.76
CH <sub>4</sub>	367	606	1081	1.78
CO <sub>2</sub>	701	837	1245	1.49
C <sub>2</sub> H <sub>4</sub>	886	941	1631	1.73

column indicates that  $\phi(r_0)$  is indeed appreciably constant for different gases, and hence we see that we have here a new method of placing the values of the internal cohesion of gases.

We get further information as to  $r_0$  and  $\delta$ , the mean effective range of molecular action from B, since

$$B = \log w, \quad \text{and} \quad w = S(\delta - \sigma).$$

If  $r_0$  (and therefore  $\delta$ ) is the same for all the molecules considered, on graphing  $w$  against  $\sigma$  we should obtain a straight line, the gradient of which is the area  $S$  of 1 grm. of the adsorbent, while the intercept on the  $\sigma$  axis is  $\delta$ , and the intercept on the  $w$  axis is  $S\delta$ , the initial volume of the surface film.

Since Van der Waal's " $a$ " has been employed for estimating the cohesion,  $\sigma$  has been recalculated from his " $b$ " by means of the relation

$$\sigma = (3b/2\pi N)^{\frac{1}{3}},$$

and the data are presented in Table XVI. The value of  $\sigma$ , calculated from the viscosity relation by Sutherland, is also given for comparison, and is denoted by  $\sigma'$ . The  $(\sigma, w)$  curve is shown in fig. 6, and the line is the most

\* 'Proc. Acad. Sci. Amsterdam,' vol. 14, p. 678.

Table XVI

Gas.	$b$ .	$\sigma$ .	$\sigma'$ .	B.	$w$ .	$\delta$ .	$\delta'$ .
A	0.00137	$2.88 \times 10^{-8}$	$2.66 \times 10^{-8}$	2.11	0.0129	$3.87 \times 10^{-8}$	$3.93 \times 10^{-8}$
N <sub>2</sub>	171	3.10	2.95	2.110	129	4.09	4.12
CO	170	3.09	2.74	2.014	103	3.88	3.68
CH <sub>4</sub>	160	3.03	—	2.068	117	3.93	—
CO <sub>2</sub>	191	3.21	2.90	2.085	122	4.15	4.01
C <sub>2</sub> H <sub>4</sub>	253	3.53	3.31	3.676	047	3.87	3.74

likely through the points shown. It will be seen that in the case of nitrogen and carbon dioxide the points lay well off the line. In the case of carbon dioxide this corresponds to the low value of  $A/a^{\frac{1}{2}}$  in Table XV, making  $\phi(r_0)$  small, and hence  $r_0$  and  $\delta$  large. The gradient of the line shown is

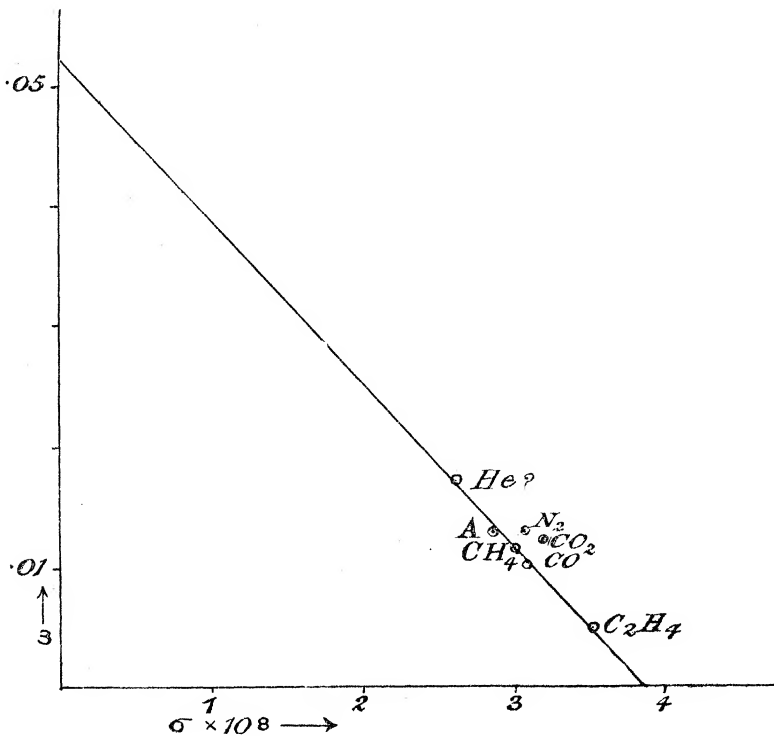


FIG. 6.

$1.31 \times 10^6$ , and hence we conclude that the area of 1 gm. of the adsorbent is  $1.31 \times 10^6$  sq. cm. Assuming the area is  $1.3 \times 10^6$  sq. cm., the author has calculated  $\delta$  in Table XVI for the various gases from the relation

$$w = S(\delta - \sigma).$$

If we use  $\sigma'$  instead of  $\sigma$ , the likeliest line gives  $S = 1.07 \times 10^6$  sq. cm., and taking this value  $\delta'$  has been calculated. It should be noted that if  $r_0$ , and therefore  $\delta$ , varies from substance to substance, the  $(\sigma, w)$  points will not lie on a straight line, but straight lines whose gradient is the value of the area  $S$  through the points in question will intercept on the  $\sigma$  axis  $\delta$  values corresponding to the various  $r_0$  values.

Our calculations, then, lead us to the conclusion that the area of 1 gm. of the charcoal used by Miss Homfray was initially  $1.3 \times 10^6$  sq. cm., and the thickness of the initial adsorption film was approximately  $4.0 \times 10^{-8}$  cm., giving the volume of this film as 0.052 c.c. If we assume the charcoal (density 1.67) to be made up of  $n$  thin laminae, the thickness  $t$  is given by the equations

$$nS't = 0.6,$$

$$2nS' = 1.3 \times 10^6,$$

whence 
$$t = \frac{1.2}{1.3} \times 10^{-6} = 90 \times 10^{-8} \text{ cm.}$$

On the other hand, if we assume the charcoal made up of  $n$  spheres of radius  $r$ , we have

$$\frac{4}{3}n\pi r^3 = 0.6,$$

$$4n\pi r^2 = 1.3 \times 10^6,$$

whence 
$$r = \frac{1.8 \times 10^{-6}}{1.3} = 140 \times 10^{-8} \text{ cm.}$$

On both assumptions we see that the thickness of the adsorbent is great compared with the adsorption layer, and hence we are justified in assuming that the adsorption film may be represented as of volume  $S \times \delta$ .

Reverting now to the points which are off the line the explanation for carbon dioxide has already been given in the low value of  $\phi(r_0)$ —the reason for this itself is not obvious. In the case of nitrogen the value of  $\phi(r_0)$  is not so low as to be attributed to the uncertainty of the  $\alpha$  values as accurate measures of the cohesion. It is therefore of interest to use the value of  $w$  corresponding to  $\sigma$  from the line in fig. 6, and see if this gives us a constant value of  $A$  in the equation

$$\log \alpha/c = \log w + A/T.$$

The values of  $w$  and  $A$ , already given, were selected as the best for reproducing the observed values. The two values of  $A$  are compared in Table XVII below.

It will be noted that the constancy of  $A$  (II) is not quite so good as that of  $A$  (I), but it is possible that more accurate observations might have led to  $A$  (II), and therefore to a more likely value of  $w$  for the  $(\sigma, w)$  curve.



Table XVII.

$$A = T (\log \alpha/c - \bar{2}.110) \quad (\text{I}).$$

$$A = 856 \quad (\text{I}).$$

$$A = T (\log \alpha/c - \bar{2}.079) \quad (\text{II}).$$

$$A = 865 \quad (\text{II}).$$

T.	A (I).	A (II).	$\Delta$ (I).	$\Delta$ (II).
194.7	857	863	1	- 2
239.4	855	863	- 1	- 2
244.5	863	871	7	6
273	857	866	1	- 1
282.3	855	864	- 1	- 1
306.5	855	864	- 1	- 1
320	844	854	-12	-11
351.2	859	871	3	6
373	857	869	1	4
			$\Sigma \Delta^2 = 208$	$\Sigma \Delta^2 = 220$

The observations on the adsorption of helium merit a brief discussion. It has already been remarked (in a footnote to Part I) that what is observed is not  $\alpha$  but  $a$ , the excess of the surface concentration over the concentration in the gaseous phase. Assuming no change in the volume of the adsorbent we have, in fact,

$$a = \alpha \left( 1 - \frac{V_a}{V} \right)$$

whence

$$a/c = \alpha/c - \alpha V_a/cV = \alpha/c - S\delta$$

and therefore

$$\alpha/c = a/c + S\delta.$$

For small values of  $a/c$  we cannot neglect  $S\delta$ . These small values only occur in the observations at higher temperatures with argon, nitrogen, and methane, and the correction does not seriously affect the results. With helium, however, the case is different. Of the observations on this gas, unfortunately only those at 83° A are sufficiently extensive to be employed. Here we have  $\log a/c = \bar{1}.81$  or  $a/c = 0.65$ . If we employ the data of Onnes (*loc. cit.*),  $T_c = 5.25$ ,  $p_c = 2.26$  atmospheres, whence  $a = 0.000069$ ,  $b = 0.00106$  leading to  $a^{\frac{1}{2}} = 0.0083$ , and  $\sigma = 2.65 \times 10^{-8}$ . We may use these values to solve for  $A/a^{\frac{1}{2}}$  in

$$\log (a/c + S\delta) = \log S(\delta - \sigma) + A/T$$

where  $S\delta = 0.052$ ,  $S\sigma = 0.035$ , leading to

$$\log (0.65 + 0.05) = \log 0.017 + A/83.$$

$$A = 83 \times (\log 0.70 - \log 0.017),$$

$$= 83 \times 1.61,$$

$$= 134.$$

Hence 
$$\frac{A}{a^{\frac{1}{2}}} = \frac{134}{0.0083} = 1.61 \times 10^4.$$

which is in good agreement with the values obtained for other gases. (The  $\sigma'$  values lead to  $1.52 \times 10^4$ .)

It is evident that if the theory holds for higher temperatures the *observed* adsorption of a gas will vanish, when

$$\log S\delta = \log S(\delta - \sigma) + A/T.$$

Thus, in the case of helium there should be no observable adsorption (or, rather, *very small negative* adsorption) after the point given by

$$\log 0.052 = \log 0.017 + 134/T,$$

or

$$T = 134/0.49 = 270,$$

and in fact Miss Homfray records zero adsorption at  $287^\circ\text{A}$  and  $290^\circ\text{A}$ .

Miss Homfray elsewhere mentions that at  $83^\circ\text{A}$ , 3 gm. of charcoal adsorbed 330 c.c. of argon at its saturation vapour pressure. Assuming the adsorbed film to have a density the same as liquid argon, we see that the volume of the film per gramme charcoal was

$$\frac{110 \times 40}{22400 \times 1.4} \quad \text{or} \quad 0.14 \text{ c.c.}$$

This is less than thrice  $S\delta$  or five times  $S\sigma$ , so we see that the transition layer between adsorbent and saturated vapour is not more than 5 molecules thick. This is what we might expect from the smallness of the value of  $\delta$ , the effective range of the molecular forces. The evidence here presented as to the value of  $\delta$  must be regarded as affording support to the views advocated amongst others by Langmuir as to the smallness of the range of molecular attraction.

#### (b) *Titoff's Observations.*

The only other set of observations which are at all extensive is due to Titoff,\* and includes data for hydrogen, nitrogen, carbon dioxide, and ammonia. Only the observations on hydrogen, nitrogen, and carbon dioxide may be used for extrapolation by means of equation (8), and the results for the two latter gases are given below in Tables XVIII and XIX :—

\* 'Zeits. f. Physikal. Chem.,' vol. 74, p. 641 (1910).

Table XVIII.

Nitrogen.  $T_c = 127$ . $B = \bar{2} \cdot 515$ .  $A = 759$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A.
194	(2.20)	2.43	+0.23	+70	714
273	1.296	1.295	-0.001	-0.2	759
303	1.019	1.020	+0.001	+0.2	759
353	0.666	0.665	-0.001	-0.2	759
424.5	0.290	0.304	+0.014	+3.3	753

Table XIX.

Carbon dioxide.  $T_c = 304$ . $B = \bar{3} \cdot 825$ .  $A = 1396$ .

T.	Log $a/c$ obs.	Log $a/c$ calc.	Divergence.	Percentage error in $a/c$ .	A.
196.5	(5.04)	4.93	-0.11	-29	1419
273	2.917	2.938	+0.021	+5.0	1390
303	2.430	2.433	+0.003	+0.7	1395
353	1.783	1.780	-0.003	-0.7	1397
424.5	1.113	1.114	+0.001	+0.2	1396

Values of  $A_0$  cannot be directly determined from the isotherms for ammonia for the reason mentioned in Part II—the  $(\alpha, \log a/c)$  curves are not straight lines. Values of  $A$  and  $B$  may, however, be determined from the isosteres for finite adsorptions as was done with argon. We have the following Table:—

Table XX.

$\alpha$ .	60	40	30	20	10	0
A	1360	1405	1428	1450	1487	1540
B	$\bar{2} \cdot 340$	$\bar{2} \cdot 268$	$\bar{2} \cdot 230$	$\bar{2} \cdot 196$	$\bar{2} \cdot 172$	$\bar{2} \cdot 150$

The zero values are extrapolated assuming no change in curvature of the  $(\alpha, A)$  and  $(\alpha, B)$  curves. But the change in curvature of the  $(\alpha, \log a/c)$  curves occurs just below  $\alpha = 10$ , and the assumption is scarcely justifiable, as the values suggested by this consideration are much lower for  $A$  and much higher for  $B$ . Nevertheless, the values given in the Table may be employed as representing a possible  $(\phi(r_0), \delta)$  configuration of the system, even if it is not the one actually occurring with ammonia at zero concentration.

The observations with hydrogen are at three temperatures only, and are

discussed after the correction  $S\delta$  to the observed  $a/c$  values has been determined. In Table XXI are presented the results already obtained. The

Table XXI.

Gas.	$a^{\frac{1}{3}}$ .	A.	$A/a^{\frac{1}{3}}$ .	$\sigma$ .	B.	$w$ .
N <sub>2</sub>	0.0518	759	$1.49 \times 10$	$3.10 \times 10^{-8}$	2.515	0.0327
CO <sub>2</sub>	837	1396	1.67	3.21	2.825	0.0067
NH <sub>3</sub>	893	1540	1.72	3.04	2.150	0.0141

( $\sigma$ ,  $w$ ) points are too few in number for an accurate determination of  $S$ , the values of  $A/a^{\frac{1}{3}}$  being uncertain, and the  $\sigma$  values close to each other. Allowing for the variation in  $A/a^{\frac{1}{3}}$ , the best value of  $S$  appears to be  $7 \times 10^6$ , while if we assume the variation in  $\delta$  from  $A/a^{\frac{1}{3}} = 1.7$  to  $A/a^{\frac{1}{3}} = 1.5$  should be the same as found with Miss Homfray's charcoal, the best value of  $S$  is  $9 \times 10^6$ . Taking  $S$  to be  $8 \times 10^6$ , we get  $S\delta$  to vary from 0.29 to 0.31. This value is so great that it is obvious that the correction must be introduced to the nitrogen and carbon dioxide values. The results are shown in Tables XVIIIA and XIXA below.

Table XVIIIA.

Nitrogen.  $T_c = 127$ . $B = 2.610$ .  $A = 736$ .

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	A.
194	(2.20)	(2.20)	2.40	696
273	1.296	1.306	1.306	736
303	1.019	1.032	1.040	734
353	0.666	0.694	0.694	736
424.5	0.290	0.354	0.344	740

Table XIXA.

Carbon dioxide.  $T_c = 304$ . $B = 3.880$ .  $A = 1377$ .

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	A.
196.5	(5.04)	(5.04)	4.89	1407
273	2.917	2.917	2.923	1375
303	2.430	2.431	2.424	1378
353	1.783	1.785	1.780	1378
424.5	1.113	1.123	1.123	1375

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The values of  $(1/T, \log a/c)$  with hydrogen do not lie on a straight line, but the curvature is less when the  $(1/T, \log a/c)$  points are considered. The value of the gradient between two of the points leads to a value of  $A/a^{\frac{1}{3}}$  much greater than any hitherto recorded, and this suggests an error in observation. The results of calculation are shown in Table XXII.

Table XXII.

Hydrogen.  $T_c = 39$ . $B = 1.11$ .  $A = 311$ .

T.	Log $a/c$ obs.	Log $a/c$ obs.	Log $a/c$ calc.	Percentage error in $a/c$ .	A.
353	1.78	1.97	1.99	+5	304
273	0.23	0.30	0.25	-12	325
194	0.66	0.68	0.71	+7	305

Table XXA presents a summary for the corrected values of A and B.  $\delta$  is calculated from the relation  $w = S(\delta - \sigma)$ , assuming  $S = 8 \times 10^6$ . Comparing the values with those in Tables XV and XVI, the tendency for the values of

Table XXA.

Gas.	$a^{\frac{1}{3}}$ .	A.	$A/a^{\frac{1}{3}}$ .	$\sigma$ .	B.	w.	$\delta$ .
H <sub>2</sub>	0.0205	311	$1.52 \times 10^4$	$2.50 \times 10^{-8}$	1.11	0.13	$4.1 \times 10^{-8}$
N <sub>2</sub>	518	736	1.42	3.10	2.61	0.041	3.6
CO <sub>2</sub>	837	1377	1.64	3.21	3.88	0.0076	3.3
NH <sub>3</sub>	893	1540	1.72	3.04	2.15	0.014	3.2

$A/a^{\frac{1}{3}}$ , and hence of  $\phi(r_0)$ , to fall with  $a$  is again to be noted, carbon dioxide not forming an exception here. This tendency points to the necessity for the existence of a second relation, presumably dynamical, connecting  $a$  and  $r_0$ . The values of  $A/a^{\frac{1}{3}}$  appear to be slightly less in the present case, indicating that the attraction of the charcoal  $a_0^{\frac{1}{3}}$  is less. This may be connected with the smaller value of  $\delta$  and the greater surface S, which leads to a smaller thickness of the adsorbent—in this case only  $13 \times 10^{-8}$  cm. if composed of thin laminae.

There are no other observations available for the purposes of the present paper, so a summary of the results may now be given.

*Summary of Part III.*

1. The form of the theoretical adsorption isostere for zero concentration has been established for a number of gases above their critical points.

2. The relationship among the constants is in good agreement with the theory based on the existence of a thin surface layer.

3. A new method of obtaining the relative internal cohesion of a gas is thereby presented.

4. The surface area of the adsorbent can be evaluated.

5. The range of molecular attraction may be determined, and in the cases considered is found to vary from 3.2 to  $4.1 \times 10^{-8}$  cm.

The author desires to express his thanks to Prof. James Walker, F.R.S., for his help in the presentation of this paper.

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*Address of the President, Sir J. J. Thomson, O.M., at the  
Anniversary Meeting, December 1, 1919.*

The losses of the Society since the last Anniversary Meeting have been very heavy. Fourteen Members on the Home List, and three Foreign Members, have died during the year, and among these are some who have for many years been most closely connected with the work of the Society, and whose discoveries and researches have for long been the glory of British science.

One of these, Sir WILLIAM CROOKES, had worked at science with untiring diligence and most conspicuous success for 60 years. A pupil of Hofmann, he became famous in 1862 by his discovery by the new method of Spectrum Analysis of a new element, thallium; this discovery won for him his election into the Society in the following year. In 1873 he again made a discovery which attracted universal attention, that of the Radiometer. The way in which he arrived at this discovery is as great a tribute to his genius as an investigator as the importance of the discovery itself. In the course of some chemical experiments, he observed certain irregularities in the weighings made with a very delicate balance; he followed these up, and at last traced them to forces acting on a surface exposed to radiation, and, with his unrivalled power of epitomising a discovery in a dramatic experiment, he summed the results of his work up in the well-known instrument, the radiometer or light-mill. Though subsequent research has not confirmed the theory by which he explained its action, the radiometer is a striking example of his skill as an experimenter, the thoroughness of his work, and his determination to leave no difficulty unsolved. His long-continued work